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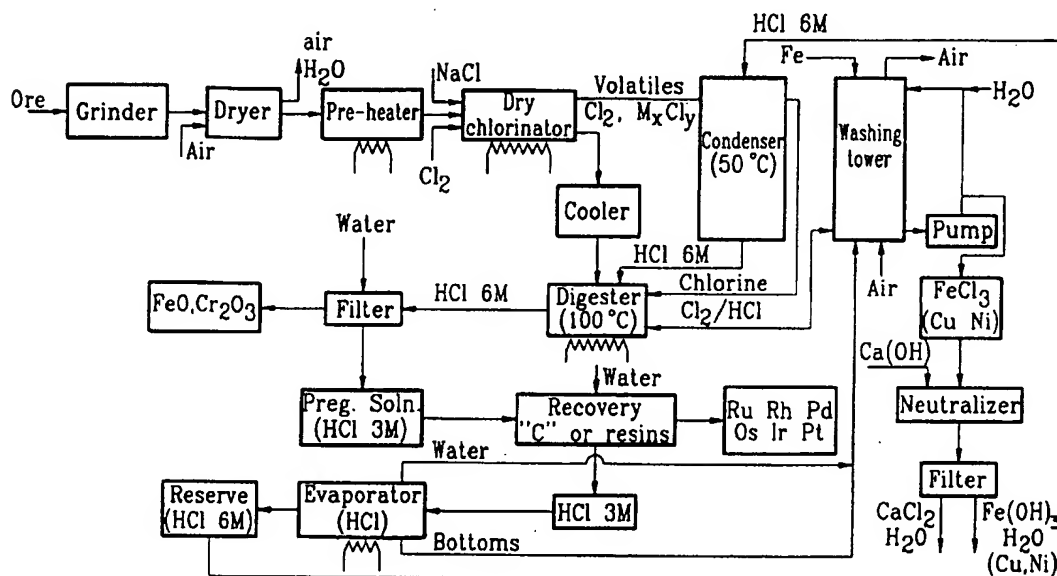
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(54) **CHLORATION A SEC DES MINERAIS OU DES CONCENTRES
DE CHROMITE CONTENANT DES PLATINOIDES**

(54) **DRY CHLORINATION OF PGM-BEARING CHROMITE ORES
OR CONCENTRATES**



(57) Processus de récupération des platinoïdes (PGM) des minerais ou des concentrés de chromite qui en contiennent, comportant les étapes suivantes : chloration à sec des minerais ou des concentrés, digestion des minerais ou des concentrés chlorés avec de l'acide chlorhydrique pour produire des sels de platinoïdes (PGM) solubles, filtration des minerais ou des concentrés de chromite insolubles résiduels pour obtenir des chromites essentiellement non altérés et une solution dense contenant des platinoïdes (PGM) et une petite quantité d'autres métaux et récupération des platinoïdes dans la solution dense.

(57) A process for recovering PGM from PGM bearing chromite ores or concentrates comprises the steps of dry chlorinating the ores or concentrates, digesting the chlorinated ores or concentrates with hydrochloric acid to produce soluble PGM salts, filtering residual insoluble chromite ores or concentrates to provide substantially unaltered chromites and a pregnant solution containing PGM and a small quantity of other metals and recovering the PGM from the pregnant solution.



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ABSTRACT

A process for recovering PGM from PGM bearing chromite ores or concentrates comprises the steps of dry chlorinating the ores or concentrates, digesting the chlorinated ores or concentrates with hydrochloric acid to produce soluble PGM salts, filtering residual insoluble chromite ores or concentrates to provide substantially unaltered chromites and a pregnant solution containing PGM and a small quantity of other metals and recovering the PGM from the pregnant solution.

TITLE OF THE INVENTION

Dry chlorination of PGM-bearing chromite ores or concentrates.

FIELD OF THE INVENTION

5 The present invention pertains to a process for recovering PGM from PGM-bearing chromite ores or concentrates.

BACKGROUND OF THE INVENTION

10 The term "Platinum Group Metals" (PGM) designates the six platinoids, namely, ruthenium, rhodium, palladium, osmium, iridium and platinum. These metals are often found together in variable proportions, and platinum normally predominates.

15 PGM are generally associated with the presence of ultramafic rocks containing agents such as nickel or chromium compounds, either sulfides or oxides. In fact, chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) has been observed to be associated with sulfides of the PGM in some important geological formations, such as the Bushveld Complex found in South
20 Africa (Merensky Reef and UG2 Chromitite).

 The current technology used for the recovery of PGM from these chromites ores calls for the grinding of the ore to about 75 microns (-200 mesh) followed in certain cases by gravity concentration and then by
25 flotation. The concentrate of the sulfides containing the PGM and other sulfides, such as iron copper and nickel sulfides, is then smelted so as to produce a matte

rich in PGM. The acid digestion of the matte leads to the individual components of the PGM after rather elaborate chemical operations.

5 The froth flotation process is a technique of general use in sulfides processing. It allows the production of base metal concentrates from ores with relatively low sulfides content. Copper and nickel productions, for example, depend upon enrichment by flotation to achieve high yield from ores having sulfide
10 contents at the level of a few percents.

In the case of the PGM, the froth collected from the flotation of the chromite ores has a PGM content of 100 to 400 ppm and incorporates copper sulfide and nickel sulfide at the percent level.

15 Because of a number of factors, the flotation of the sulfides from chromite ore is rather delicate and much influenced by variations in ore composition induced by oxidation, occlusion in chromite (coarse grinding) and other variables responsible for the modifications of the
20 surface of the particles. Although nominal recovery of the order of 80% are reported for the flotation of the PGM and associated sulfides from chromite ores, the actual practice can lead to significantly lower figures, and constant adjustment of the operational parameters are
25 required. This situation and the fact that some types of PGM-bearing minerals cannot be floated readily makes

desirable the investigation of alternate methods for the recovery of PGM from chromite ores.

5 The analytical procedures for the determination of PGM as generally practiced call for the oxidation of the substrate in the presence of aqua regia, a mixture of hydrochloric and nitric acids, the presence of a free halogen, such as chlorine, being required for the more refractory elements of the group (see J.C. Van Loon and R.R. Barefoot, *Determination of the Precious Metals*, pp. 10 55,101, John Wiley & sons, 1991). Another approach calls for a fusion with nickel sulfide followed by acid digestion of the melt under oxidizing conditions. Such procedures are deemed fairly efficient in converting all of the PGM in the form of soluble complexed chlorides 15 that can be determined in solution by instrumental analysis.

It will be obvious that such approaches, although appropriate for analytical purposes, cannot be retained for industrial production. The amount of 20 chemicals required for the total digestion of the PGM ore would render the cost of the operation absolutely prohibitive. Chromite ores contains typically from 20 to 30 percent chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$) associated with 3-4 ppm of PGM. Since the standard oxidizing agents cited above 25 are reported as strong enough to oxidize readily the iron oxide and trivalent chromium oxide of the chromite, the consumption of oxidizer per unit weight of PGM would

become so high as to remove any profitability from the process.

5 The examination of the chemical literature concerning the oxidation of ferrous oxide or trivalent chromium oxide is quite convincing to the effect that oxidizing agents strong enough to oxidize PGM will very readily oxidize ferrous oxide or trivalent chromium oxide to ferric oxide and hexavalent chromium oxide.

10 Ferrous oxide is readily oxidized by air in the presence of acids such as nitric acid or hydrochloric acid (see S.M. Latimer, *The oxidation state of the elements*, 2nd ed., p. 224, Prentice-Hall, 1952). Even chromite itself, $\text{FeO} \cdot \text{Cr}_2\text{O}_3$, is reported oxidized by air, which is a much milder oxidizer than chlorine or nitric acid. This reaction is the industrial method of
15 preparation of sodium chromate:

$$2 \text{FeO} \cdot \text{Cr}_2\text{O}_3 + 4\text{Na}_2\text{CO}_3 + 3.5\text{O}_2 \rightarrow 4\text{Na}_2\text{CrO}_4 + 4\text{CO}_2 + \text{Fe}_2\text{O}_3$$

(see H. Remy, *Treatise on Inorganic Chemistry*, Vol. II, p. 155, Elsevier Publishing Company, 1956).

20 STATEMENT OF THE INVENTION

While attempting to purify PGM-bearing chromites from the base metal components, the inventors have found that, under appropriate conditions, chlorine could react with the PGM in chromites without significant
25 attack on chromite itself. This result, unexpected from the statements of the chemical literature as indicated

above, opens the way to a new approach to the recovery of PGM from chromite ores.

The present invention therefore relates to a process for the recovery of PGM from PGM bearing chromite ores or concentrate which comprises the steps of:

- dry chlorinating the ores or concentrates to produce chlorinated ores or concentrates;
- digesting the chlorinated ores or concentrates with hydrochloric acid to produce soluble PGM salts;
- filtering residual insoluble chromite ores or concentrates to provide substantially unaltered chromites and a pregnant solution containing PGM and a small quantity of other metals; and
- recovering PGM from the pregnant solution.

If chlorine is present in the digesting step, the reaction is facilitated.

In one form of the invention, the dry chlorinating step is carried out at temperatures from 350°C to 800°C.

In another form of the invention, the dry chlorinating step is conducted in the presence of sodium chloride.

In another form of the invention, the ores or concentrates are heated prior to the dry chlorinating

step if the heat of reaction of chlorine with the substrate is not sufficient to promote the reaction.

5 The inventors have found that if the treated material is a concentrate containing relatively large amounts of sulfides and PGM as compared to the starting ore, the reaction of chlorine with said concentrate is so exothermic as to generate on site most or all of the energy required to initiate the reaction. Under such conditions, the initial temperature can be much lower
10 than 350°C, some reaction being observed on the material at room temperature.

The invention presents several advantages over the pyrometallurgical approach currently used for the recovery of PGM from chromite ores, namely:

15 - the preparation of a concentrate by flotation is not required (although a concentrate could still be used, if available, with the present invention). This step, which relies on physical properties of the ore (surface characteristics and size of sulfide particles),
20 calls for constant adjustments for the flotation, and some ores are not amendable to it;

- the percentage of recovery of PGM is from 10 to 20% higher than what is obtained in practice with the pyrometallurgical approach;

25 - the osmium which is almost completely lost in the pyrometallurgical approach is largely recovered in the condenser of this process.

- the circuit of the present invention is less elaborate than the pyrometallurgical circuit, no recycling of slag or chemical digestion of matte being required to reach the stage of dissolved PGM; and

- 5 - the present invention can be operated on a modular basis and is less capital incentive than the pyrometallurgical approach.

10 Other objects and further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. It should be understood, however, that this detailed description, while indicating preferred embodiments of the invention, is given by way of illustration only, since various changes and modifications within the spirit
15 and scope of the invention will become apparent to those skilled in the art.

IN THE DRAWINGS

20 Figure 1 is a block diagram illustrating the various steps of one embodiment of a dry chlorination of chromite ores made in accordance with present invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

25 First, the ore is reduced to an appropriate size. It will be readily understood that too coarse a material will prevent access to the values inside the particles and will slow down the reaction. On the other

hand, very fine grinding involves significant cost. A value of particles from 75 microns to 45 microns appears as a practical compromise between reactivity and cost of grinding.

5 This finely ground material is then dried to
less than 0.1% of free water and heated up to the
appropriate temperature for the dry chlorine treatment.
This temperature of dry chlorination has been found to be
variable depending on the refractoriness of the ore under
10 treatment. With certain ores, a temperature of 450°C has
been sufficient to recover more than 90% of the PGM. In
other instances, higher temperatures (up to 700°C) have
been required to achieve similar recovery. The
temperature of dry chlorination is an important factor in
15 the capacity of treatment of a given apparatus. This
temperature must be high enough to ensure the desired
reactions with the PGM, while too high a temperature may
prove detrimental to the equipment and may induce
undesirable reactions with chromite. If the variations
20 of reactivity of the ores are taken into account, it has
been found that a range of temperature from 350°C to
800°C allows to obtain good reactivity, leading to high
percentage of extraction of PGM while limiting to
acceptable values the side reactions with chromite. The
25 ground ore can be heated to the selected temperature
prior to contacting with chlorine or heated up in the
chlorinator itself. Both procedures have been tried but
the preheating approach turned out to be simpler, a
rotary kiln or a fluidized bed being favored.

The hot ore is then introduced in the dry chlorinator, which is kept at the selected temperature, and a slow stream of chlorine is circulated through the mass at constant temperature. It must be noted that the amount of chlorine required is very small and amounts from 1.0 to 1.5 times the combined chlorine in the course of the dry chlorination. The amount of chlorine consumed by the PGM is relatively negligible, the consumption being related to the amount of reacting chromite and base metals, such as iron, nickel and copper present in the starting ore. As an indicative estimate, it can be said that some of the base metals (Cu, Ni) at most a few percents of the iron in the chromite and less than one-tenth of one percent of the chromium in the chromite will be converted into the corresponding soluble chlorides. In order to ensure an homogeneous distribution of the chlorine through the reacting mass, the chlorine stream can be diluted by a carrier gas, such as nitrogen for example. The dry chlorination can be achieved on a continuous basis or batch-wise by simple percolation through the mass of the reacting gas or by the fluidization of the reacting bed or by renewal of the surfaces in a rotating kiln. The contacting time required is relatively long, of the order of half an hour to two hours, depending on the nature of the ore, the temperature used and, to some extent, on the granulometry of the ore. For sake of simplicity of an apparatus which operates under rather aggressive conditions (chlorine at 600°C for example), a static bed of appropriate thickness has been found convenient. Since the material to be

treated is to be loaded hot, the heating of the dry chlorination reactor has to be just enough to compensate for heat losses of the system.

5 The volatiles leaving the dry chlorinator are directed to a condensing tower and quenched by a spray of hydrochloric acid at a concentration of 6M. The temperature in this tower is of the order of 50°C and the condensable are collected and carried down by the acid spray.

10 The solid left in the dry chlorinator after treatment is dumped after cooling in a digester containing the acid from the spray in the condensing tower, and is further digested, at 100°C, for one to several hours, the stirring of the mass being ensured by
15 recirculation of the off gases of the condensation tower through the slurry. The off gases from the digester, mostly nitrogen, hydrochloric acid vapors, chlorine and traces of sulfur compounds, are directed back to a gas treatment system after recycling condensed hydrochloric
20 acid to the digester.

 The temperature and duration of digestion in hydrochloric acid in the presence of chlorine must be adjusted in such a fashion as to ensure the complete solution of the PGM. The heat increases the rate of such
25 reactions, which would proceed nevertheless at room temperature but at a slower rate.

For sake of completeness of dissolution as readily as possible of the PGM, hot treatment is preferred over cold treatment and a one to several hours of contacting is retained.

5 The dry chlorination, followed by digestion, has now transformed more than 90% of the PGM into soluble chlorinated entities. The addition of some sodium chloride in the system has produced soluble chlorides with some of the PGM that would otherwise give insoluble
10 chlorides. In the case of iridium, for example, this metal gives a trichloride with chlorine at 500°C, but this salt is not water-soluble. However, in the presence of sodium chloride, at 600°C, the action of chlorine on Ir leads to sodium hexachloroiridate Na_2IrCl_6 , a soluble
15 salt. A similar behavior is noted with rhodium and ruthenium (see J.C. Van Loon et al, cited above).

The pregnant solution is then separated from the insoluble chromite ore by filtration and the cake is submitted to several washings in order to minimize the
20 retention of the valuable species. After the rinsing operations, the acid concentration in the pregnant solution is of the order of 3 molar.

The recovery of valuable species from this solution can be achieved by a variety of techniques, such
25 as precipitation over activated carbon, or circulation over ion-exchange resins. The resulting depleted solution is directed to a distillation line in order to

recycle the hydrochloric acid at a concentration of 6M which corresponds to the azeotropic composition of the HCl-H₂O system. The bottoms of this distillation contain the iron, the chromium and the base metals (Ni, Cu, etc...) that have been dissolved in the course of the digestion of the dry-chlorinated ore. This material is directed to the gas treatment system which also receives the vapors of the digester.

The entities found at the inlet of the purification system are oxidizing by nature (Cl₂) and acidic. They also include all the ions liberated by the digestion. This mixture is reduced by percolation over iron filling, and the acidic lixiviate is neutralized with limestone. Under alkaline conditions, base metal oxides are precipitated as hydroxides; hexavalent chromium, after reduction, is precipitated by the relatively large amounts of trivalent iron present, and the chlorine ends up as calcium chloride. The resulting slurry can be filtered and calcium chloride eliminated as solid after saturation of the circuit with this salt.

Referring to TABLE 1, six examples are given to illustrate the implementation of the invention. The PGM-bearing chromite ore (100 g) is reduced to the appropriate size, heated up at an appropriate temperature with or without addition of salt, in the presence of chlorine, and then digested in 6M hydrochloric acid for a determined period of time. The reacting mass is then filtered and rinsed; the filtrate, after removal of

excess hydrochloric acid, is contacted with either activated carbon or ion-exchange resins to recover PGM. The analyses are done by ICP-MS technique.

5 In the case of Example 2, the pregnant solution after filtration of the insolubles contained 30 ppm of chromium and 50,000 ppm of iron. The acid was fractionated by distillation and the bottoms treated by a slight excess of limes so as to give a neutral filtrate and a solid cake where ferric hydroxide predominates.

10 In another embodiment of the present invention, the finely ground and dried material to be treated is a concentrate containing relatively large amounts of sulfides and PGM as compared to the starting ore. When the chlorine is added to this concentrate, the reaction
15 is so exothermic as to generate on side most or all of the energy required to initiate reaction. Accordingly the concentrate can be preheated to a temperature which is much lower than 350°C. Indeed under certain circumstances, there can be reaction on the material at
20 room temperature.

Although the invention has been described above with respect with one specific form, it will be evident to a person skilled in the art that it may be modified and refined in various ways. It is therefore wished to
25 have it understood that the present invention should not be limited in scope, except by the terms of the following claims.

TABLE I

Examples No	Source of ore (chromite)	Particle size (micron)	Dry chlorination			Digestion		PGM*	
			Temp. (°C)	Duration (hr.)	NaCl	Temp. (°C)	Duration (hr.)	Initial (ppm)	Recovery (%)
1	Coleraine Canada	75	350	1.0	no	100	3	4.50	86
2	Coleraine Canada	45	450	1.5	no	100	5	4.50	96
3	Eastern Platinum South Africa	75	350	1.0	no	100	4	4.507	50
4	Eastern Platinum South Africa	75	450	1.0	no	100	4	4.507	76
5	Eastern Platinum South Africa	45	660	1.5	yes	100	3	4.507	96
6	Eastern Platinum South Africa	45	670	1.5	yes	100	4	4.507	97

* Total values for Pt, Pd, Rh, Ru, Ir, Re

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The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for recovering PGM from PGM-bearing chromite ores or concentrates, comprising the steps of:

- dry chlorinating said ores or concentrates at temperatures from 350°C to 800°C to produce chlorinated ores or concentrates;
- digesting said chlorinated ores or concentrates with hydrochloric acid in the presence of chlorine to produce insoluble PGM salts;
- filtering residual insoluble chromite ores or concentrates to provide substantially unaltered chromites and a pregnant solution containing PGM and a small quantity of other metals; and
- recovering PGM from said pregnant solution.

2. A process as defined in claim 1, wherein the dry chlorinating step is carried out at temperature from 350°C to 800°C.

3. A process as defined in claim 1, wherein the dry chlorinating step is conducted in the presence of sodium chloride.

4. A process as defined in claim 1 or 2, comprising the step of heating said ores prior to said dry chlorinating step.

5. A process as defined in claim 4, comprising the step of grinding said chromite ores to a size of about 45 microns before the heating step.

6. A process as defined in claim 3, comprising the step of cooling said chlorinated ores prior to the digesting step.

7. A process as defined in claim 6; wherein said digesting step is carried out in the presence of heat.

8. A process as defined in claim 1, comprising the step of condensing volatiles created by the dry chlorinating step, said volatiles including volatile salts of PGM.

9. A process as defined in claim 8, wherein the condensing step is conducted by quenching said volatiles with a spray of hydrochloric acid.

10. A process as defined in claim 9, wherein said condensing step is carried out at a temperature in the order of 50°C.

11. A process as defined in claim 9, further directing said spray of hydrochloric acid to the digesting step.

12. A process as defined in claim 11, wherein said digesting step is conducted in the presence heat in the order of 100°C.

13. A process as defined in claim 1, wherein gases resulting from the digesting step are directed to a gas treatment system after recycling condensed hydrochloric acid to the digesting step.

14. A process as defined in claim 1, wherein said recovering is carried out by precipitating said pregnant solution over activated carbon.

15. A process as defined in claim 1, wherein said recovering step is carried out by circulating said pregnant solution over ion-exchange resins.

16. A process as defined in claim 14 or 15, further comprising the step of distillating a depleted solution resulting from the recovering step to thereby recycle the hydrochloric acid; the bottoms of said distilating step being directed to a system for treating vapours from the digesting step.

